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AUTHOR(S): R. D. Taylor and J. N. Farrell

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Los Alamos, New Mexico 87545

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MOSSBAUER EFFECT OF EUROPIUM METAL UNDER PRESSURE

R. D. Taylor and J. N. Farrell*

Physics Division, Los Alamos National Laboratory

Los Alamos, NM 87545

ABSTRACT

The pressure dependence of the magnetic hyperfine field and of the isomer shift of ^{151}Eu in europium metal has been studied in a diamond anvil pressure cell at low temperatures. In the pressure range 0 - 12 GPa at 44 K (T_N = 90 K) the magnetic hyperfine field changes from -22 T to -8 T while the isomer shift increases from -7.3 to -3.8 mm s^{-1} relative to a SmF_3 source. The changes are interpreted as indicative of a pressure driven intermediate valence state causing a reduced magnetic moment in Eu. Intermediate valence and magnetic order coexist over the range of pressures studied.

INTRODUCTION

Intermediate valency in rare earth systems has been extensively studied for over a decade.[1,2] Intermediate valency (IV) results from a rapid fluctuation between two valence state configurations that are nearly degenerate. Changes in IV can be associated with temperature, with pressure, and with substitutional alloying. A myriad of fascinating material properties arise in IV systems. Oftimes the two valence states involve a magnetic and a non-magnetic ground state. For example, Eu^{2+} compounds are magnetic and Eu^{3+} compounds are non-magnetic. Eu metal orders antiferromagnetically with a $T_N \sim 90$ K and is in the Eu^{2+} state at ordinary pressures.[3] One of the important questions is whether an IV system can order magnetically.[4] A recent study of the pressure-induced breakdown of magnetic order (MO) of Eu^{2+} in $Eu(Pd_{0.8}Au_{0.2})Si_2$ suggested there might be a small region of coexistence of MO and IV.[5] Other Eu-based systems and Sm-based systems have shown an apparent incompatibility between IV and MO.[1]

We have measured the Mossbauer Effect (ME) of ^{151}Eu in Eu metal for pressures up to 23 GPa at room temperature and up to 14 GPa for $4 < T < 120$ K. The ME gives simultaneously the isomer shift (related to the valence) and the hyperfine field (related to the magnetization). The ^{151}Eu ME is particularly suitable for these studies. The ME lifetime is relatively long so that only an average of the IV fluctuations is seen. Eu^{2+} compounds have an isomer shift of -13.4 to -7.3 mm/sec, and Eu^{3+} compounds have a shift of 0 to + 1.7 mm/sec, relative to a SmF_3 source. A well resolved ME spectrum is obtained for the hyperfine fields typically found in magnetically ordered Eu systems. We interpret our results as direct evidence for the coexistence at low temperatures of IV and MO over a wide range of pressure.

EXPERIMENT

A 150-mCi $^{151}SmF_3$ source having an active diameter of 4 mm was used as the parent for the ^{151}Eu ME. The Eu metal absorber was cut from a fresh surface of a large piece of high purity Eu metal (Ames Laboratory). The 50-μm-thick sample was placed in a 300-μm hole in a $Ta_{90}W_{10}$ gasket prepressed to a thickness of 80-μm for use in a Merrill-Bassett-type diamond anvil pressure cell.[5] The sample was sealed off under liquid argon to provide an inert hydrostatic pressure medium. Pressures were determined <u>in situ</u> by the ruby fluorescence method.[5] The gasket material provided effective collimation of the 21.5-keV ME gamma rays. The pinhole sample size resulted in low counting rates necessitating long counting times, about one day per datum. A conventional, constant acceleration ME spectrometer was used. The source and absorber were held at the same temperature in a cryostat that reached 44 K using pumped solid nitrogen. Data were analyzed using Lorentzian line shapes and the appropriate magnetic Hamiltonian for a polycrystalline sample. A single linewidth, centroid (isomer shift), intensity, and splitting (hyperfine field) parameter characterize each ME spectrum. Spectra at 44 K are shown in Fig. 1 for three pressures and 44 K. In this range, the magnitude of the (negative) hyperfine field decreases and the isomer shift increases with pressure.

RESULTS AND DISCUSSION

The isomer shift with pressure at 44 K is shown in Fig. 2. Data at 4 K parallel the same curve. The initial slope, 0.38 mm sec^{-1} GPa^{-1}, is somewhat lower than that reported[6] for pressure data below 1.6 GPa; they interpreted the isomer shift simply as a congruent compression of the s-conduction electrons. We believe a substantial part of the shift from -7.3 mm s^{-1} at ambient pressure

to -3.7 mm s^{-1} at 12.1 GPa is due to a valence shift (IV). PV relations for Eu to 30 GPa[7] have also supported the idea that Eu metal undergoes at least a partial $Eu^{2+} \rightarrow Eu^{3+}$ transition.

The hyperfine field at 44 K as a function of pressure is given in Fig. 3. Data at 4 K lie predictable higher; T_N varies little with pressure.[8] Thus the decrease in the magnitude of the hyperfine is not due to a change in T_N, rather it is due to a reduction in the average magnetic moment of the Eu atoms as a result of the change in average valence toward non-magnetic Eu^{3+}. Attempts to drive the hyperfine field to zero were thwarted by a crystallographic phase transition[7] near 12.5 GPa.

Although it is not possible at present to quantify the degree of the $Eu^{2+} \rightarrow Eu^{3+}$ transformation (a simple interpolation of the ME data suggest $Eu^{+2.5}$ at 12.1 GPa), we feel the results show coexistence of magnetic order and intermediate valence in Eu metal over a wide range of pressure.

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*Present address at Teledyne Brown Engineering, Huntsville, Alabama.

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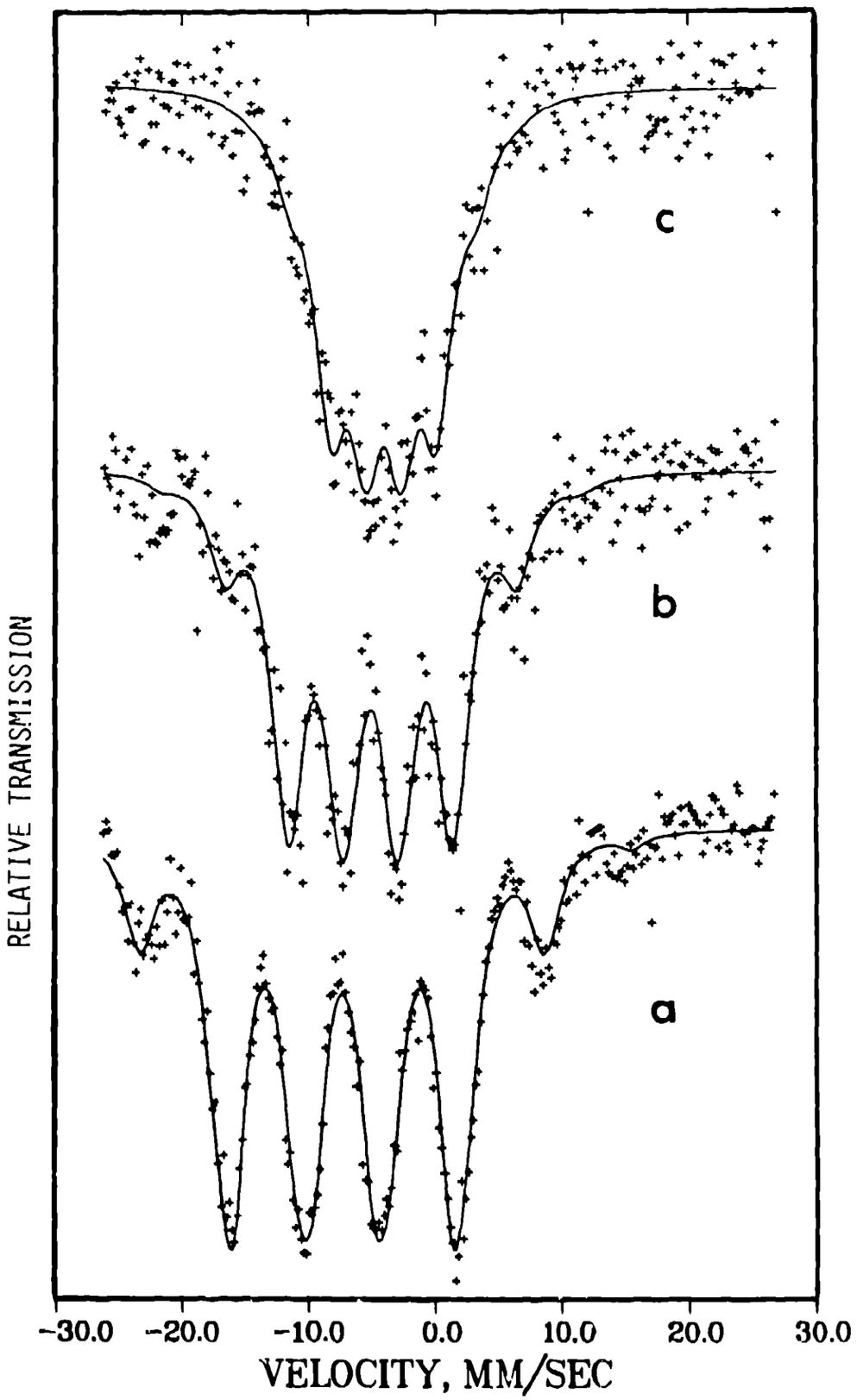
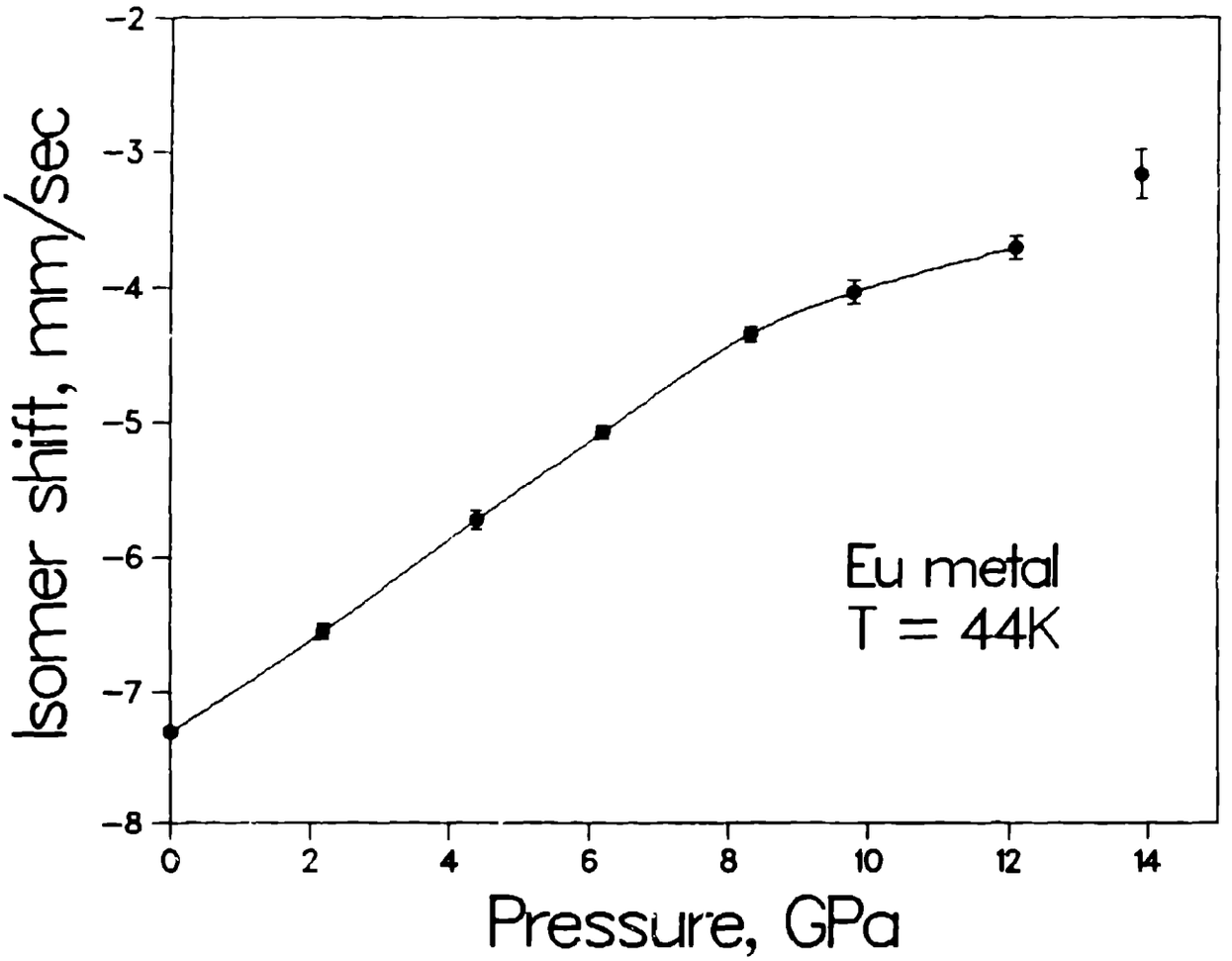
Figure Captions

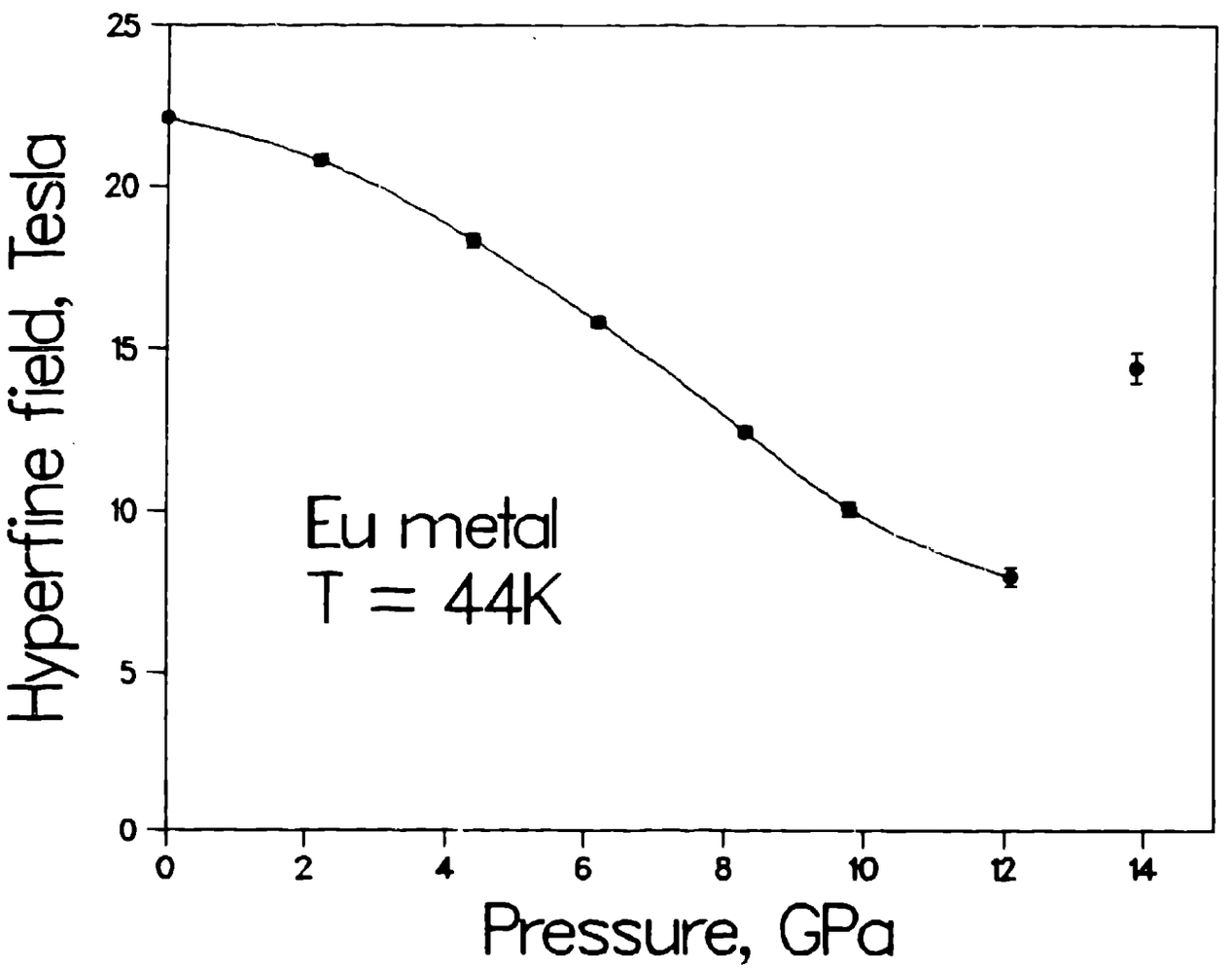
Fig. 1. ^{151}Eu Mossbauer spectra of Eu metal at 44 K and a) 0, b) 6.2, and c) 9.8 GPa. Note the change in the centroid and in the splitting.

Fig. 2. Mossbauer isomer shift of ^{151}Eu in Eu metal as a function of pressure. The SmF_3 source and the absorber are at 44 K.

Fig. 3. Pressure dependence of the magnetic hyperfine field at the ^{151}Eu nucleus in Eu metal at 44 K. T_N is near 90 K at these pressures. Near 12.5 GPa a crystallographic phase transition occurs at room temperature.


c
b
a
RELATIVE TRANSMISSION
-30.0
-20.0
-10.0
0.0
10.0
20.0
30.0
VELOCITY, MM/SEC


Isomer shift, mm/sec
−2
−3
−4
−5
−6
−7
−8
0
2
4
6
8
10
12
14
Pressure, GPa
Eu metal
T = 44K


Hyperfine field, Tesla
25
20
15
10
5
0
0
2
4
6
8
10
12
14
Pressure, GPa
Eu metal
T = 44K